

## Super Tough Carbon Nanotube Composite Fibers for Electronic Textiles

The energy needed to break spider silk is a hundred times larger than to break the same weight steel wire.<sup>1,2</sup> This property, called toughness, has inspired commercialization efforts, from pulling silk from spiders a century ago<sup>3</sup> to genetically engineering silk protein production in goat's milk today<sup>1</sup>. While individual carbon single walled nanotubes (SWNTs) have much higher Young's modulus, strength, and toughness than spider silk<sup>4,5</sup>, these properties have not been realized for continuous nanotube fibers. We describe spinning hundred-meter-long carbon nanotube composite fibers having a tensile strength matching spider silk and a toughness far exceeding spider silk, previous carbon fibers, or synthetic organic fibers. We make fiber supercapacitors from our spun fibers and weave them into textiles.

Our spinning method builds upon the pioneering discovery by Vigolo *et al.*<sup>6</sup> of coagulation-based nanotube spinning. Their process involves injecting surfactant-dispersed SWNTs into a rotating bath of aqueous polyvinyl alcohol (PVA) to produce nanotube gel fibers, which are washed to desorb PVA and surfactant<sup>7,8</sup>. Too weak to be easily handled, these gel fibers are pulled from the coagulation bath at ~1 cm/min to form solid nanotube fiber some tens of centimeters long<sup>8</sup>.

We report continuous processes for making a reel of spun nanotube gel fiber and then for converting this gel fiber into a hundred meter length of solid nanotube fiber at >70 cm/min. The spinning solution is injected from a needle into the center of a cylindrical pipe in which the PVA coagulation solution flows. Contact with the coagulant collapses the spinning solution into a nanotube/PVA gel fiber, which moves down the pipe for winding on a mandrel. Using SWNTs made by the HiPco process<sup>9</sup> and lithium dodecyl sulfate surfactant, optimizing the flow rates of spinning and coagulation solutions, and making no effort to remove PVA from the gel, we obtain gel fibers having the mechanical strength needed for the second part of the spinning process. This continuous second step involves unwinding the gel fiber onto a series of godets that carry it through an acetone washing bath, a path length for drying, and then to wrapping the solid fiber on a mandrel. The presently described ~50 micron diameter fibers contain ~60% by weight SWNTs.

We observe (Fig. 1a) that these SWNT composite fibers have a toughness exceeding 570 J/gm and a tensile strength (1.6 GPa) matching the toughest spider silk<sup>2</sup> (~1.4 GPa). This ultimate tensile strength is over  $10^4$  times higher than for “dry-spun” carbon nanotube fibers<sup>10</sup> and seven times higher than recently reported<sup>7</sup> for drawn coagulation-spun nanotube fibers. Our pre-drawn fibers match the energy absorption capability of spider silk up to the breaking strain of the toughest silk (30%), and continue absorbing energy until reaching an energy-to-break (570 J/gm) that is much higher than spider dragline silk<sup>2</sup> (165 J/gm), Kevlar fiber<sup>2</sup> (33 J/gm), and previous coagulation-spun nanotube fibers<sup>7</sup> (1.7 J/gm). This toughness results from the present combination of high strength and high strain to failure, whose uniqueness is illustrated in Fig. 1b. The Young’s modulus (80 GPa) near failure stress is twice that recently reported<sup>7</sup> for drawn coagulation-spun SWNT fibers and equal to that of directly synthesized 20 cm SWNT strands<sup>11</sup>, which have ~1.2 GPa strength and low toughness. Normalized to density, our nanotube composite fibers have over twice the Young’s modulus and tensile strength of strong steel wire<sup>1</sup> and ~700 times the toughness. The present combination of very high failure strain and strength is not found for other reported nanotube composites, even when loaded with above 50% nanotubes<sup>12,13</sup>. While very strong, high modulus PVA fibers can be obtained by ultra-drawing at high temperatures, they have much lower toughness than our nanotube composite fibers.

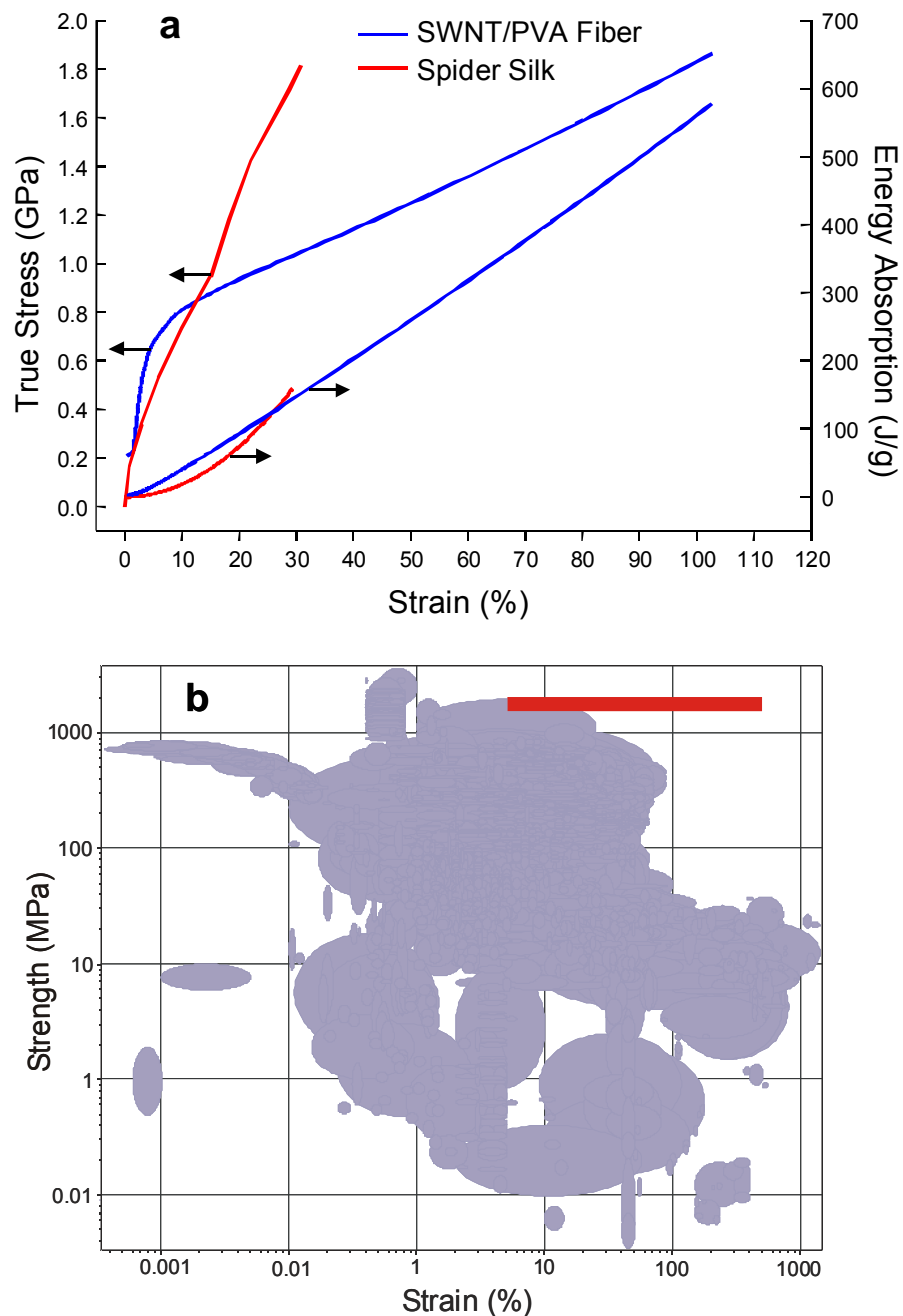
The elongation needed for toughness is enabled by the absence of measurable fiber necking during deformation. This stability against failure by the magnification of incipient necking suggests that the strain rate is approximately linearly dependent on the applied stress (Newtonian flow), which we confirmed by direct stress-strain measurements. PVA coats the nanotubes, according to scanning electron micrographs, providing an important interphase region between the nanotubes and the surrounding, largely amorphous PVA. The toughness of spider silk arises from chain extension in amorphous regions between relatively rigid crystalline protein blocks<sup>1</sup>, and we believe that amorphous PVA between SWNTs serves a similar function for our composite fibers.

We used our spun nanotube fibers to make supercapacitors and wove them into textiles (Fig. 2). Two nanotube composite fibers were separately coated with electrolyte (by dipping in an aqueous PVA/phosphoric acid mixture), twisted together, and then recoated

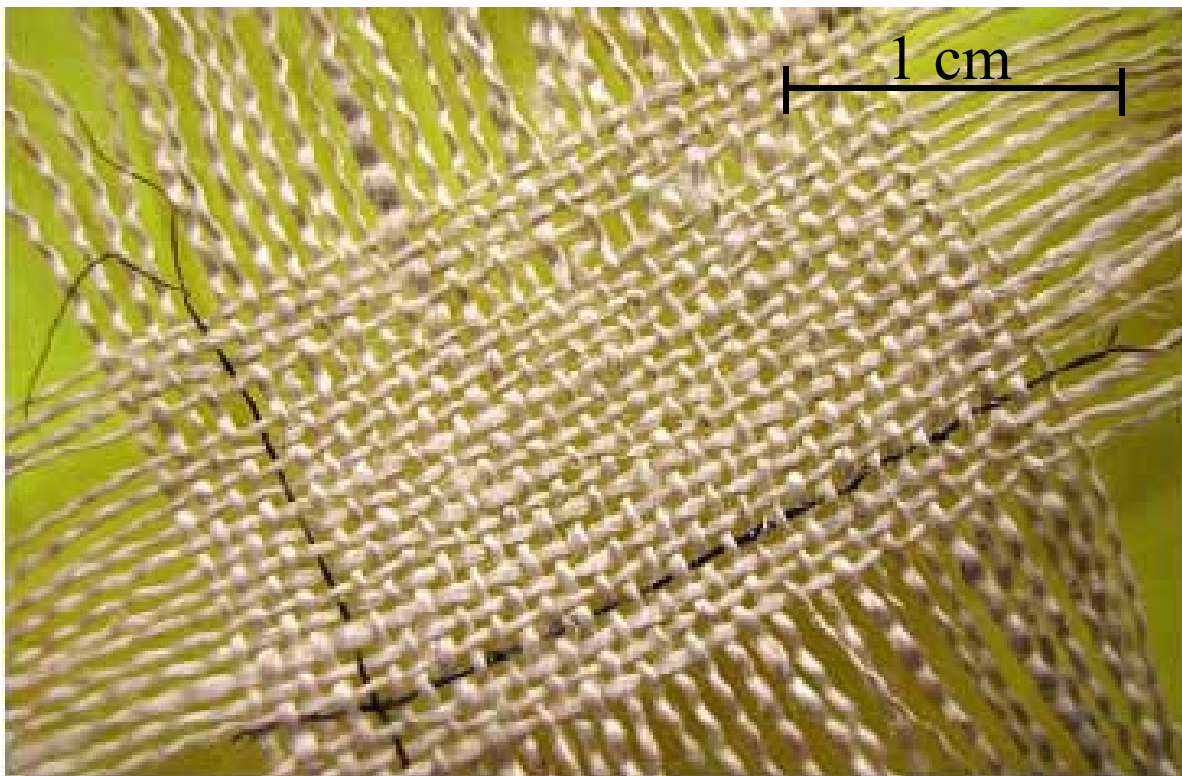
with electrolyte. This 100  $\mu\text{m}$  diameter fiber supercapacitor provided a capacitance (5 F/gm) and energy storage density (0.6 Wh/kg at one volt) comparable to large commercial supercapacitors and unchanged performance over the measured 1200 charge/discharge cycles. Other electronic textile applications also seem promising for these nanotube fibers, which are easily woven or sewn into textiles - such as distributed sensors, electronic interconnects, electromagnetic shielding, antennas, and batteries.

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1. Kubik, S., *Angew. Chem. Int. Ed.* **41**, 2721-2723 (2002).
  2. Vollrath, F. & Knight, D. P., *Nature* **410**, 541-548 (2001).
  3. Notes (author unknown), *Nature* **59**, 81 (1898).
  4. Walters, D. A. *et al.*, *Appl. Phys. Lett.* **74**, 3803-3805 (1999).
  5. Yu, M.-F., Files, B. S., Arepalli, & S., Ruoff, R. S., *Phys. Rev. Lett.* **84**, 5552-5555 (2000).
  6. Vigolo, B. *et al.*, *Science* **290**, 1331-1334 (2000).
  7. Vigolo, B, Poulin, P., Lucas, M., Luanois, P., & Bernier, P., *Appl. Phys. Lett.* **81**, 1210-1212 (2002).
  8. Poulin, P., Vigolo, B., Launois, P., *Carbon* **40**, 1741-1749 (2002).
  9. Nikolaev, P. *et al.*, *Chem. Phys. Lett.* **313**, 91-97 (1999).
  10. Jiang, K., Li, Q., & Fan, S., *Nature* **419**, 801 (2002).
  11. Zhu, H. W. *et al.*, *Science* **296**, 884-886 (2002).
  12. Shaffer, M. S. P. & Windle, A. H., *Advanced Materials* **11**, 937-941 (1999).
  13. Mamedov, A. A. *et al.*, *Nature Materials*, Advanced Online Publication (2002).



**Figure 1** Mechanical property comparisons. **a**, True stress and energy absorption versus strain for high toughness spider silk<sup>2</sup> and a pre-drawn nanotube composite fiber. The pre-draw to 194% strain required 210 J/gm. The energy-to-break during the subsequent 104% elongation of the pre-drawn nanotube composite fiber was 570 J/gm, versus a total energy-to-break of 165 J/gm for the spider silk fiber. **b**, The strength and failure strain for the nanotube composite fiber type of part **a** for different degrees of initial pre-draw (red line) and the three thousand materials of all types (lavender field) in the Cambridge Materials Selector data base ([www.grantadesign.com](http://www.grantadesign.com)).



**Figure 2** Photograph of a textile containing two nanotube fiber supercapacitors woven in orthogonal directions. The helically wound nanotube fibers are separated at the capacitor ends, so that electrical connections can be made.